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L3: Entry 2 of 7

File: USPT

Feb 15, 2000

DOCUMENT-IDENTIFIER: US 6025479 A

TITLE: Method of preparing water swellable gel from chitin

Brief Summary Text (8):

Chitin films have also been referred to in literature. Methods of preparing chitin films vary in terms of casting solution, coagulating agent and/or drying method employed. A chitin membrane was prepared by coagulation of a dimethylacetamide/N-methylpyrrolidone/LiCl solution of chitin using 2-propanol, followed by immersion of the membrane in water (S. Aiba et al in Preparation and Properties of Dialysis Membranes, Chitin in Nature and Technology, Ed. R. Muzzarelli, C. Jeuniaux, G. W. Gooday, Plenum Press, New York, 1986, p. 396 prepared). Chitin films have also been prepared by pressing a powdered sample at room temperature followed by heat-treatment in vacuum at 50.degree. C. for three days (M.Kakizaki et al in Molecular Motion and Dielectric Relaxation in Chitin and Acylchitins, Chitin in Nature and Technology, Ed. R. Muzzarelli, C. Jeuniaux, G. W. Gooday, Plenum Press, New York, 1986, p. 39). A chitin film has also been prepared by casting a solution of chitin in N,N dimethylacetamide/5% LiCl and allowing evaporation of the solvent, leading to coalescence of the film (Rutherford and Dunson in The Permeability of Chitin Films to Water and Solutes, Chitin, Chitosan and Related Enzymes, Ed. J. P. Zikakis, Academic Press, New York, 1984, p.136). The coalesced film was washed in acetone and water, blot dry, placed between paper towels and pressed in a book.

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L14: Entry 8 of 21

File: USPT

Sep 5, 2000

DOCUMENT-IDENTIFIER: US 6113794 A

TITLE: Composite solvent resistant nanofiltration membranes

Abstract Text (2):

(a) a substrate ultrafiltration membrane formed from an ethylenically unsaturated nitrile, such as acrylonitrile and substituted acrylonitrile polymers, and

Brief Summary Text (5):

In general, there are many references that employ polyacrylonitrile (PAN), substituted PAN or PAN co-polymers as a substrate UF membrane. In most cases, PAN is modified e.g. by crosslinking or by hydrophilization.

Brief Summary Text (6):

Many of these references also include at least one additional layer, which is often cross-linked in situ, and involve a plurality of method steps.

Brief Summary Text (7):

For example, Nawawi and Huang.<sup>sup.1</sup>, generally discloses composite chitosan based membranes made by forming a substrate membrane by casting a solution of the polymer onto a plate to form a porous membrane film, coating chitosan on the substrate membrane and cross-linking the chitosan in situ.

Brief Summary Text (8):

The use disclosed for this composite membrane is for pervaporation (PV) of feed with high isopropanol content. It is noted that pervaporation is quite different from nanofiltration. Pervaporation is carried out at reduced pressure, while nanofiltration is effected at positive pressure and the fluxes are orders of magnitude higher. Additionally, selective layer in a PV membrane is dense while it is porous in a NF membrane.

Brief Summary Text (9):

The reference also discloses the use of only polysulfone as the polymer for substrate membrane and hexamethylene diisocyanate (HMDI) as the cross-linking agent. Notably, this cross-linker is cytotoxic. It is interesting to note that the concentrations of HMDI and glutaraldehyde required for killing 50% test animals after a 4 h inhalation period were 0.31 and 5000 ppm, respectively. It is obvious that the toxicity of HMDI is significantly greater than glutaraldehyde.

Brief Summary Text (10):

Also, it is emphasized that the concentration of chitosan used is low i.e. 0.5%/w. This results in a low viscosity of coating solution and the formation of a dense thin film. At higher concentrations of chitosan, a porous layer is formed.

Brief Summary Text (11):

Further, in Wang et al..<sup>sup.2</sup>, a composite chitosan membrane is disclosed wherein the microporous substrate membrane is PAN and the top layer is chitosan. It is noted that the PAN is hydrolyzed with NaOH. Cross-linking between the PAN and chitosan layers also includes a middle intermolecular layer.

Brief Summary Text (12):

The hydrolysis of the surface of the PAN is to facilitate the reaction of PAN and chitosan, so that tighter bonding between the two layers will occur.

Brief Summary Text (14):

In U.S. Pat. No. 4,985,138, which was issued on Jan. 15, 1991 to M. Pasternak, the substrate layer is PAN and the coating layer is PEI, cross-linked in situ by urea or amide linkages e.g. a polyisocyanate or a poly (carbonylchloride).

Brief Summary Text (15):

Specifically, the composite membrane includes a substrate of a homo- or co-polymer of PAN, which is cross-linked, and a coating of an ionically charged hydrophilic, cross-linked polymer. An additional intermediate coating layer is also present.

Brief Summary Text (22):

a substrate ultrafiltration membrane formed from an ethylenically unsaturated nitrile polymer, such as polyacrylonitrile and substituted polyacrylonitrile, and

Brief Summary Text (27):

(b) casting the solution onto a support to form a UF membrane substrate, and

Brief Summary Text (28):

(c) coating the UF membrane substrate with an aqueous solution of a hydrophilic polymer containing reactive functional groups, the concentration of the polymer in solution being 1.5-2.5% w/w, and a weak acid or a buffer containing a weak acid and its corresponding salt, to adjust the pH to 3-5.

Brief Summary Text (35):

The substrate membrane may be supported on a porous support, such as those fabricated from non-woven or woven cellulosics, polyethylene, polyesters such as polyethylene terephthalate, polytetrafluoroethylene, glass fibers, porous carbon, graphite, inorganic supports based on alumina and/or silica. The substrate membrane may be fabricated into any desired shape, e.g. a hollow fiber, flat sheet or tubular.

Brief Summary Text (36):

Coating on the substrate membrane may be carried out by immersion, spraying or casting a coating solution. The final thickness of the coating may, for example, lie within the range of from about 1 to about 500 nm.

Brief Summary Text (38):

the membrane morphology and its flux and rejection properties (e.g. acetone, ethanol, methanol, formamide, water, sodium dodecyl sulfate, divalent salts such as zinc chloride, calcium chloride, magnesium perchlorate and monovalent salts such as lithium nitrate, lithium chloride). The casting solution may be filtered by any of the known processes (e.g. pressure filtration through microporous filters, or by centrifugation). It is then cast onto a non-woven or woven porous substrate selected from cellulosics, polyethylene, polyesters such as polyethylene terephthalate, polytetrafluoroethylene, glass fibers, porous carbon, graphite, inorganic supports based on alumina and/or silica. The membrane may also be formed as a hollow fiber or tubelet which does not require a support for practical use; or the support may be of such shape, and the membrane is cast internally thereon. The concentration of polymer in the casting solution may vary as a function of its molecular weight (MW) and additives, and may be for example, within the range of about 5-25% w/w, preferably about 10-20% w/w. The casting solution temperature may vary from about 10-60.degree. C., preferably about 20-40.degree. C., depending on the particular polymer, its molecular weight, the cosolvents and additives in the casting solution.

Brief Summary Text (39):

The casting solution may be applied to the above-mentioned supports or porous substrates by any of the well-known techniques of casting. The wet film thickness may lie within the range of 100-400 .mu.m, preferably 150-250 .mu.m for flat sheet membranes; tubular membranes may have thicker walls. The cast film of polymer solution may be immersed immediately, or after a partial drying for 5 seconds to 5 minutes under ambient conditions or at elevated temperature, in a gelation bath of a non-solvent. Non-solvent bath may comprise water, to which there may optionally be added a small percentage of a solvent and/or surfactant (e.g. sodium dodecyl

sulfate). The bath temperature may be maintained at 0-40.degree. C., preferably at 15-25.degree. C. Thus membranes having a thickness of 50-300 .mu.m, preferably of 50-150 .mu.m can be formed. Instead of polyacrylonitrile itself, substituted polyacrylonitriles, e.g. C.sub.1 -C.sub.6 alkylacrylonitriles such as methacrylonitrile and hexylacrylonitrile polymers may alternatively be used as membrane forming material.

Brief Summary Text (40):

The substrate membrane is then coated with an aqueous solution of a polymer selected from hydrophilic polyfunctional oligomers or polymers containing active hydrogen atoms bound to oxygen or nitrogen atoms. The pH of this solution is adjusted to 3-5, by means of a weak acid or a buffer containing a weak acid and its corresponding salt. The examples of such hydrophilic polymers include polymers with amino groups such as chitosan and its derivatives with degree of deacetylation ranging from 70-100 and molecular weights ranging between 20,000-2,000,000, preferably between 50,000-150,000.

Brief Summary Text (41):

The coating solution may have a polymer concentration in the range of 1.5-2.5% w/w, preferably in the range of 2-2.5% w/w. Weak acids including carboxylic acids such as acetic acid, citric acid, lactic acid or the buffer of these acids with their salts e.g. sodium acetate, may be used as solvents. The wet coating layer thickness may be in the range of 50-300 .mu.m, preferably in the range of 50-150 .mu.m. Note that the wet thickness is different than the final dry thickness of the coating layer. These coated membranes are then dried at 25-70.degree. C., preferably at 30-50.degree. C. for 10-30 h, preferably 20-25 h.

Detailed Description Text (2):

Polyacrylonitrile (Polysciences Inc., USA), MW 150,000, was dissolved in DMF and was cast onto a moving nonwoven polyester and gelled in reverse osmosis (RO) water at 25.degree. C. After washing overnight with water, the substrate membrane showed 38% rejection for polyethylene oxide (MW 100 kDa) and pure water flux of 200 liters per square meters per hour (LMH) at 200 kPa. It was then coated with 2.5% w/w Chitosan solution (in 0.3 M acetic acid/0.2 M sodium acetate buffer) using a glass rod and dried at 50.degree. C. for 24 h in a convection oven. These coated and dried membranes were then treated with 4% w/v aqueous sodium hydroxide to convert Chitosan acetate to Chitosan. The postcoating crosslinking was carried out by immersing these composite membranes in aqueous solution of glutaraldehyde (0.02% w/w) at 25.degree. C. for 30 minutes. These membranes after washing several times with water exhibited pure water flux of 17 LMH at 480 kPa and MWCO of 700 Daltons. The observed rejections for salts and sugars for these membranes are shown in Table 1.

CLAIMS:

1. A nanofiltration composite membrane comprising a substrate ultrafiltration membrane formed from non-cross-linked ethylenically unsaturated nitrile polymer, and a porous coating of a cross-linked hydrophilic polymer having a molecular weight of 20,000 to 2,000,000 and containing reactive functional groups, formed from an aqueous solution of the polymer containing 1.5-2.5% w/w of the polymer.

4. A composite membrane according to claim 3, wherein the substrate membrane is configured in a form selected from the group consisting of a flat sheet, tubular, hollow fiber and spiral.

10. A method according to claim 9, wherein the substrate membrane is configured in a form selected from the group consisting of a flat sheet, tubular and hollow fibres, and wherein membrane modules of a type selected from the group consisting of including plate and frame, tubular, spirals and hollow fibres are made from one of the configurations.

12. A method for making a nanofiltration membrane, comprising

(a) providing a solution of a non-cross-linked ethylenically unsaturated nitrile polymer in an organic solvent,

(b) casting the solution onto a support to form a UF membrane substrate,

(c) coating the UF membrane substrate with an aqueous solution of a hydrophilic polymer having a molecular weight of 20,000 to 2,000,000 and containing reactive functional groups, the concentration of the polymer in solution in step (c) being 1.5-2.5% w/w, and

(d) cross-linking the reactive functional groups of the hydrophilic polymer in situ, wherein the cross-linking is effected by a substantially non-cytotoxic cross-linking agent selected to provide chemical stability and pH stability below pH 7.

19. A method according to claim 18, wherein the substrate is polyacrylonitrile and wherein the cross-linking agent is glutaraldehyde.

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## Freeform Search

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US Pre-Grant Publication Full-Text Database  
JPO Abstracts Database  
EPO Abstracts Database  
Derwent World Patents Index  
IBM Technical Disclosure Bulletins

**Term:**

110 and substrate and layer

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### Search History

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result set

*DB=USPT; PLUR=YES; OP=OR*

<u>L14</u>	l10 and substrate and layer	21	<u>L14</u>
<u>L13</u>	L11 and acetyl chloride	1	<u>L13</u>
<u>L12</u>	L11 and acetic anhydride	3	<u>L12</u>
<u>L11</u>	L10 and composite	13	<u>L11</u>
<u>L10</u>	chitosan membrane	44	<u>L10</u>
<u>L9</u>	L3 and chitosan and composite and substrate	1	<u>L9</u>
<u>L8</u>	L7 and composite	1	<u>L8</u>
<u>L7</u>	L3 and chitin and aceti?	4	<u>L7</u>
<u>L6</u>	L4 and aceti?	3	<u>L6</u>
<u>L5</u>	L4 and acetylated	0	<u>L5</u>
<u>L4</u>	L3 and chitosan	7	<u>L4</u>
<u>L3</u>	((210/500.29)!.CCLS. )	260	<u>L3</u>
<u>L2</u>	L1 and "n-acetylated"	0	<u>L2</u>
<u>L1</u>	membrane and chitosan and acetylated	1	<u>L1</u>

END OF SEARCH HISTORY

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☐ 1. Document ID: US 6174443 B1

L12: Entry 1 of 3

File: USPT

Jan 16, 2001

US-PAT-NO: 6174443

DOCUMENT-IDENTIFIER: US 6174443 B1

**\*\* See image for Certificate of Correction \*\***

TITLE: Purification of wheat germ agglutinin using macroporous or microporous filtration membrane

DATE-ISSUED: January 16, 2001

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Ruckenstein; Eli	Amherst	NY		
Zeng; Xianfang	Cary	NC		

US-CL-CURRENT: 210/651; 127/34, 210/638, 210/650, 530/414

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
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K00C

☐ 2. Document ID: US 6153749 A

L12: Entry 2 of 3

File: USPT

Nov 28, 2000

US-PAT-NO: 6153749

DOCUMENT-IDENTIFIER: US 6153749 A

TITLE: Process for the preparation of acylated hexaazaisowurtzitane derivatives

DATE-ISSUED: November 28, 2000

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Kodama; Tamotsu	Kurashiki			JP
Minoura; Haruyuki	Kurashiki			JP
Miyake; Nobuhisa	Kurashiki			JP
Yamamatsu; Setsuo	Kurashiki			JP
Katsumata; Tsutomu	Yokohama			JP

US-CL-CURRENT: 540/556; 149/92, 540/554

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
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K00C



Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
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K/MC

☐ 3. Document ID: US 4714555 A

L6: Entry 3 of 3

File: USPT

Dec 22, 1987

US-PAT-NO: 4714555

DOCUMENT-IDENTIFIER: US 4714555 A

TITLE: Agent for separation

DATE-ISSUED: December 22, 1987

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Shibata; Tohru	Himeji			JP
Okamoto; Ichiro	Himeji			JP

US-CL-CURRENT: 210/635; 210/198.2, 210/198.3, 210/500.29, 210/644, 210/656, 210/658, 502/404

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
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K/MC

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L4 and aceti?

3

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L6: Entry 1 of 3

File: USPT

Dec 4, 2001

US-PAT-NO: 6325218

DOCUMENT-IDENTIFIER: US 6325218 B1

**\*\* See image for Certificate of Correction \*\***

TITLE: Polyion complex separation membrane with a double structure

DATE-ISSUED: December 4, 2001

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Lee; Jung Min	Daejeon			KR
Yeom; Choong Kyun	Daejeon			KR
Kim; Chul Ung	Daejeon			KR
Kim; Beom Sik	Daejeon			KR
Kim; Kwang Joo	Daejeon			KR

US-CL-CURRENT: 210/490; 210/500.29, 210/500.35, 210/500.37, 210/500.41, 210/500.43,  
427/244, 427/245

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	Claims	KMC
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☐ 2. Document ID: US 5993661 A

L6: Entry 2 of 3

File: USPT

Nov 30, 1999

US-PAT-NO: 5993661

DOCUMENT-IDENTIFIER: US 5993661 A

**\*\* See image for Certificate of Correction \*\***

TITLE: Macroporous or microporous filtration membrane, method of preparation and use

DATE-ISSUED: November 30, 1999

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Ruckenstein; Eli	Amherst	NY		
Zang; Xianfang	Buffalo	NY		

US-CL-CURRENT: 210/651; 210/231, 210/490, 210/500.23, 210/500.29, 210/500.42,  
210/636, 264/200, 264/41

☐ 3. Document ID: US 5993661 A

L12: Entry 3 of 3

File: USPT

Nov 30, 1999

US-PAT-NO: 5993661

DOCUMENT-IDENTIFIER: US 5993661 A

**\*\* See image for Certificate of Correction \*\***

TITLE: Macroporous or microporous filtration membrane, method of preparation and use

DATE-ISSUED: November 30, 1999

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Ruckenstein; Eli	Amherst	NY		
Zang; Xianfang	Buffalo	NY		

US-CL-CURRENT: 210/651; 210/231, 210/490, 210/500.23, 210/500.29, 210/500.42,  
210/636, 264/200, 264/41

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	KWC
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